



# Synthesis of nitrogen and lanthanum codoped barium titanate with a novel thermal ammonolysis reactor



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## ABSTRACT

Lanthanum doped barium titanate was nitrated by thermal ammonolysis with a newly designed reactor, which performs extended efficiency to supply ammonia with less decomposition at elevated temperatures above 600 °C. The kinetics of nitrogen-uptake was studied systematically at elevated temperatures. Nitrogen-content, thermal stability and crystallographic phase of nitrated lanthanum doped barium titanate were characterized by several techniques. The final nitrogen-content of nitrated lanthanum doped barium titanate was much higher than the content of lanthanum, resulting in the formation of oxygen vacancies compensating the additional negative electrical charge of nitrogen anions occupying regular oxygen sites in the lattice. Through thermal ammonolysis, strongly reducing conditions because of the decomposition of ammonia generating hydrogen gas causes the formation of barium orthotitanate as a secondary phase. Ammonolysis temperature below 800 °C and suppression of thermal decomposition of ammonia gas are essential to realize a nitrated lanthanum doped barium titanate as a single phase.

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## 1. Introduction

Tuning of the physical properties in electroceramics based on barium titanate BaTiO<sub>3</sub> is generally achieved by compositional or microstructural design, e.g. acceptor- or donor-doping [1–4], the use of nano-powders [5]. Such compositional design is mainly realized by substitutional chemical modifications on the cationic sites of Ba<sup>2+</sup> and Ti<sup>4+</sup>, but not on the anionic site of the perovskite lattice. In recent years perovskite-related oxides with a partial substitution of oxygen by nitrogen, referred to as oxynitrides, are increasingly stimulating interest due to their unusual characteristics making them attractive for applications like non toxic pigments [6], photocatalysts for water splitting [7], giant permittivity [8] and giant magnetic resistance [9]. Although there are some examples of nitrogen-doped functional electroceramics reported in the lit-

erature [10–12], the total number of published studies is rather small since the field is still quite new. Especially regarding the material synthesis of barium titanate which is massively applied on an industrial scale into passive electronic components especially as insulating multilayered co-fired ceramic capacitors (MLCC) [13] and semiconducting thermistors showing a positive temperature coefficient of resistance (PTCR) [14] less information is available [15,16]. Therefore the questions, to what extent oxygen may be exchanged by nitrogen in barium titanate and how this substitution affects the crystallography, conductivity and dielectric characteristics of barium titanate based materials is highly relevant not only to the fundamental but also to the technological point of view.

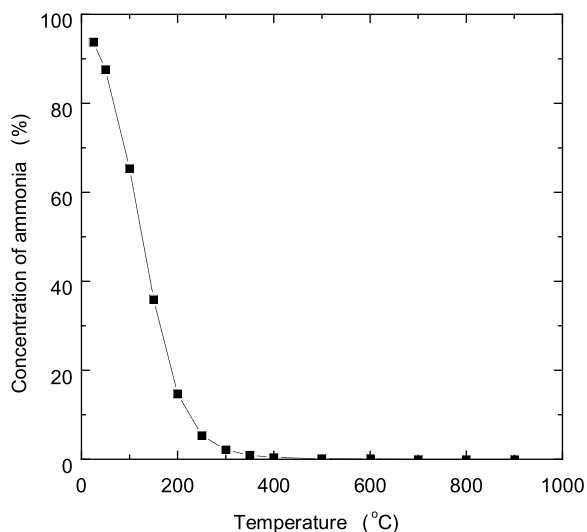
Most widely ammonia is used for nitridation of perovskite-related oxides at high temperatures (600 °C–1200 °C) [17]. In this temperature range the rapid decomposition of ammonia NH<sub>3</sub> into hydrogen H<sub>2</sub> and nitrogen N<sub>2</sub> strongly limits the effectiveness of the nitridation reaction. At 600 °C, for example more than 99.8% of ammonia decomposes under conditions of thermodynamical equilibrium at standard pressure. This is illustrated in Fig. 1, showing the temperature dependence of the concentration of undecomposed ammonia [18] according to the relation:



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**Fig. 1.** Temperature dependence of concentration of ammonia under conditions of thermodynamical equilibrium at standard pressure.

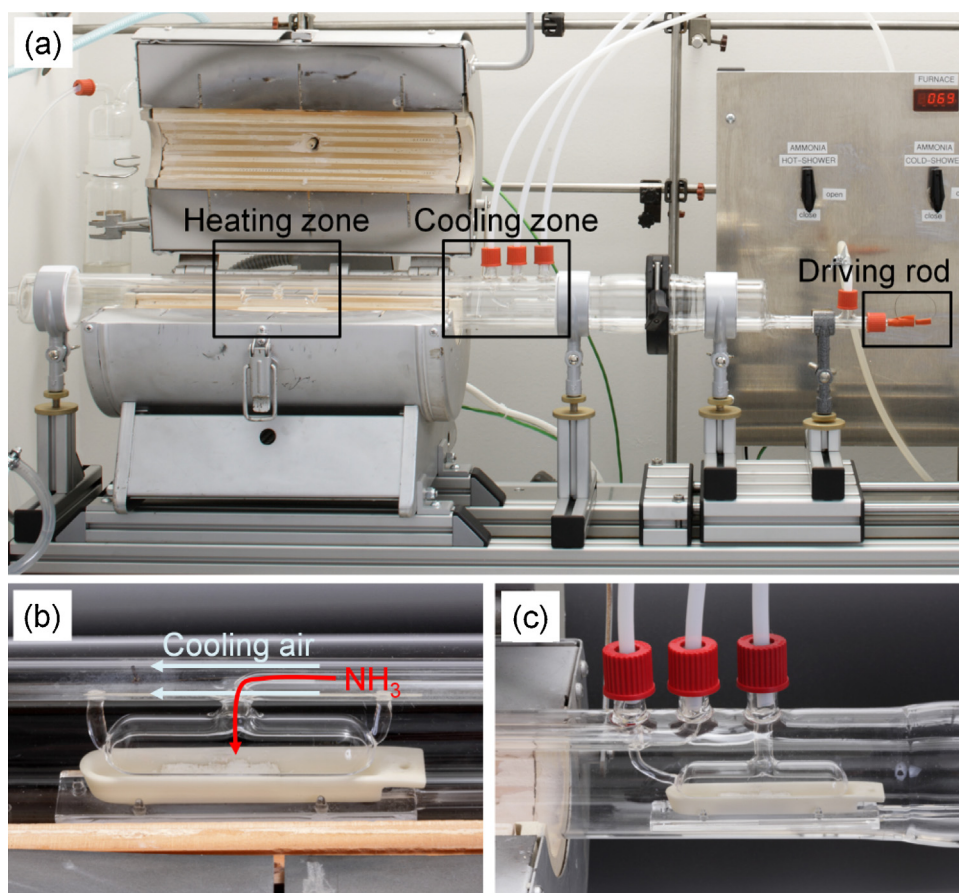
Two strategies are known to improve the efficiency of the ammonolysis reaction. The first one is achieved by increasing the reactivity of ammonia, e.g. by plasma gasification, and the second one is realized by suppressing the decomposition of ammonia. Although it is known that microwave induced ammonia plasma improves the ammonolysis reaction [17], this method is at present not applicable for large scale ammonolysis processes because of

its poor scalability. Therefore we designed and constructed an ammonolysis reactor to suppress the decomposition of ammonia at elevated temperatures. In this study we investigated the influence of the nitridation parameters (temperature, ammonia flow rate and reaction time) on phase purity, crystallography and nitrogen-content of La-doped barium titanate powders. These ceramic compositions are possibly technically relevant to eventual applications as semiconducting donor doped PTC-thermistor components, those need acceptor compensation in the form of oxygen exchange by nitrogen balancing the loss of oxygen that results from firing in reducing conditions. In this case  $\text{La}^{3+}$  cations substituting  $\text{Ba}^{2+}$  cations on the regular A-sites of the perovskite lattice are electrically equalizing the negative surcharge caused by  $\text{N}^{3-}$  that replace  $\text{O}^{2-}$  ions.

## 2. Experimental procedure

### 2.1. Sample preparation

The nitridation process of La-doped barium titanate  $\text{Ba}_{0.997}\text{La}_{0.003}\text{TiO}_3$  was studied in the powdery state in order to achieve an as homogeneous nitrogen uptake as possible. For the preparation of barium titanate powder, the conventional mixed oxide route was used. Commercial grade of  $\text{BaCO}_3$  ( $\geq 99\%$  pure, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany),  $\text{TiO}_2$  ( $\geq 99.9\%$  pure, Sigma-Aldrich) and  $\text{La}_2\text{O}_3$  (Alfa Aesar GmbH & Co., KG, Karlsruhe, Germany) as a dopant were milled with yttria-stabilized zirconia (YSZ) balls and 2-propanol for 6 h on a roller bench. After milling and separation from the balls, the resulting slurry was dried in a rotary evaporator and calcined at  $1150^\circ\text{C}$  for



**Fig. 2.** Illustration of the thermal ammonolysis reactor, (a) overall image, magnified image of (b) the heating zone inside the tube furnace, and (c) the cooling zone outside of the furnace on the right side.

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